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A NEW METHOD FOR THE SYNTHESIS  
OF PERFLUORO- $\beta,\beta$ -DIMETHYLACRYLONITRILE

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ADA197985

# REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  CRDEC-TR-88106			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION  CRDEC		6b. OFFICE SYMBOL (if applicable) SMCCR-RSC-O	7b. ADDRESS (City, State, and ZIP Code)		
6c. ADDRESS (City, State, and ZIP Code)  Aberdeen Proving Ground, MD 21010-5423			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION CRDEC		8b. OFFICE SYMBOL (if applicable) SMCCR-RSC-O	10. SOURCE OF FUNDING NUMBERS		
8c. ADDRESS (City, State, and ZIP Code)  Aberdeen Proving Ground, MD 21010-5423			PROGRAM ELEMENT NO.	PROJECT NO. 1L161102	TASK NO. A71A
11. TITLE (Include Security Classification)  A New Method for the Synthesis of Perfluoro- $\beta$ , $\beta$ -Dimethylacrylonitrile					
12. PERSONAL AUTHOR(S) Hydro, William R.; King, James W., Ph.D.; and King, Cliff R., Ph.D.*					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 85 Aug to 85 Dec		14. DATE OF REPORT (Year, Month, Day) 1988 May	
15. PAGE COUNT 21					
16. SUPPLEMENTARY NOTATION *Dr. Cliff R. King is employed at the University of Maryland, College Park, MD 20742.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Acetonitrile, Crown Ether Fluorocyanolefin		
07	03		Catalyst GLC Analyses PFIB		
15	02		Concentration Profile NMR Spectra (continued on reverse)		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  The title compound was prepared in modest yield by treatment of perfluoroisobutylene (PFIB) in acetonitrile solvent with potassium cyanide in the presence of 18-crown-6 ether catalyst. Product formation in the time course of the reaction was observed to follow a Gaussian rather than a plateau profile; maximum concentration occurred between 60 and 70 min with incomplete conversion of the PFIB. A major by-product of the reaction was tentatively identified as a condensation product of the PFIB and title compound. Reaction mechanisms consistent with experimental results are proposed to explain product and by-product formation. Suggestions for further work are proposed.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>		
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON			22b. TELEPHONE (Include Area Code) (301) 671-2914		22c. OFFICE SYMBOL SMCCR-SPS-T

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

18. SUBJECT TERMS (Continued)

Potassium Cyanide  
Organofluorine Compounds,  
Partition Coefficient,  
Reaction Mechanisms,  
Reaction Optimization,

*Chemical Reactions*

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## PREFACE

The work described in this report was authorized under Project No. 1L161102A71A, Research in Chemical and Biological Defense, Chemical Warfare and Smoke. This work was started in August 1985 and completed in December 1985. The experimental data are recorded in laboratory notebook No. 8113.

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## Acknowledgments

The authors thank William Beaudry and Linda Szafraniec for determining and interpreting NMR spectra; Michael W. Ellzy for assisting with GLC analyses; Drs. A.J. Muller and H.S. Aaron, and Leonard Szafraniec and Ronald J. Kassel for helpful discussions and suggestions. The encouragement and general support of C. Parker Ferguson and Dr. John F. Weimaster are also sincerely appreciated.



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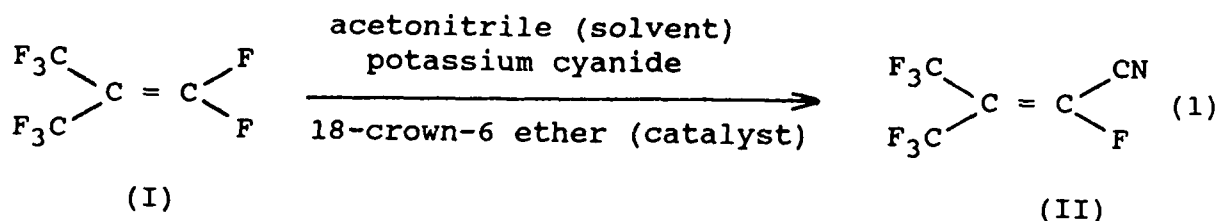
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A NEW METHOD FOR THE SYNTHESIS  
OF PERFLUORO- $\beta$ , $\beta$ -DIMETHYLACRYLONITRILE

1. INTRODUCTION

The replacement of one or more hydrogen atoms in an organic compound by fluorine atoms usually modifies not only the physical properties of the compound but also may significantly change its pharmacological profile as well.<sup>1,2</sup> Such alterations of properties and/or bioactivities are essential considerations of investigations directed to the design or discovery of new physiologically active compounds. When these new compounds are mono- or polyfluorinated analogs of known entities, and direct synthesis from the latter is difficult to achieve, the challenge becomes the functionalization of an appropriate fluorinated starting material; often, fluoroalkenes can serve this purpose. As an example of this concept, the synthesis of the title compound (1,1,1-trifluoro-2-trifluoromethyl-3-cyano-3-fluoro-2-propene) (II) has been reported to proceed by treatment of perfluoroisobutylene (PFIB) (I) with sodium cyanide in dioxane containing a small amount of water.<sup>3</sup> In our hands this model reaction gave water soluble products rather than the desired compound, and therefore the objective of this work became the development of an alternate method of synthesis. For this purpose we chose to retain PFIB as the starting material and to take advantage of the ability of crown ethers to catalytically generate reactive "naked" cyanide ion in anhydrous acetonitrile.<sup>4</sup> The overall reaction may be represented as



2. EXPERIMENTATION AND RESULTS

2.1 Materials and Equipment.

The materials and equipment used in the experiments described herein are those found in well-equipped organic synthesis laboratories and generally available from commercial suppliers. Perfluoroisobutylene was purchased from Armageddon Chemical Company, 431 Salem Street, Durham, NC 27703.

### 2.1.1 Distillation Column.

The fractional distillations required in these experiments were performed with a glass column consisting of two joined sections, the lower of which was 3-1/2 in. high by 12 mm o.d., containing 1/8-in. glass helices. The upper section was 7-1/2 in. high by 12 mm o.d., and contained 1/16-in. glass helices. There is no special significance to either height, diameter, or packing of this column. Any column of similar dimensions and packing should be appropriate.

### 2.1.2 Chromatographic Instrumentation.

Gas-liquid chromatographic (GLC) analyses were performed on a Varian Model 6000 instrument operating in the thermal conductivity detector (TCD) mode and using a Shimadzu C-R1B recorder-integrator. The analytical column was 1/8-in. by 12-ft stainless steel containing 10% Silastic 420 (DC-LSX-3-0295) liquid phase on 80/100 mesh Gas Chrom Q-II support. The instrument operating parameters were:

Sample Size: 0.2  $\mu$ L

Injector temperature: 220 °C

TCD oven temperature: 280 °C

TCD filament temperature: 300 °C

Detector range: 0.5

Attenuation: 8

Helium flow rate: 30 mL/min

Temperature program for the column oven:

Initial temperature: 36 °C; hold for 10 min after injection.

Program from 36 to 120 °C at 15°/min; hold for 4 min.

### 2.1.3 NMR Instrumentation.

NMR spectra for pertinent nuclei were determined on Varian Instrument Group spectrometers as:

$^1\text{H}$  - Model EM 390

$^{19}\text{F}$  - Model FT 80A

$^{13}\text{C}$  - Model XL 200

## 2.2 Synthesis of Perfluoro- $\beta,\beta$ -Dimethylacrylonitrile.

The reaction apparatus for this procedure consisted of a 250-mL, 3-neck, round-bottom flask equipped with a mechanical stirrer, thermometer, and reflux condenser cooled with a Dry-Ice/acetone mixture to minimize loss of PFIB (boiling point 5 °C) and product (boiling point 47 °C) during the reaction. Samples for GLC analysis are noted parenthetically.

A solution of 71.6 g (0.36 mole) of PFIB in 140 mL of acetonitrile containing 0.140 g (0.2% by weight of the PFIB) of 18-crown-6 ether, was cooled to -10 °C and treated with 25.9 g (0.40 mole) of potassium cyanide. The resulting mixture was stirred at -10° to +2 °C for 60 min (Sample 1, Table 1). The reaction mixture was then poured into an ice-cold solution of 40 mL of concentrated sulfuric acid in 360 mL of water; to the latter was added 200-mL of cold water washings of the reaction flask. The quenched mixture, which now consisted of an upper aqueous layer and two oily lower layers, was transferred to a separatory funnel. The lower oily layers were separated together and filtered through a loose glass wool plug to remove a small amount of white solid residue; after standing for 2 hr, the layers were separated. The lower layer was light green in color and weighed 68.5 g (Sample 2, Table 1); the upper layer was a dark medium red weighing 10.0 g (Sample 3, Table 1).

The lower oil layer was treated with 10 mL of cold, concentrated sulfuric acid to again give a 3-phase mixture, the lower phase being the acid. The middle layer (the largest of the three) was cloudy white, while the small upper layer was clear and red in color (Sample 4, Table 1). The unseparated mixture was then rapidly flash distilled (no column) over a period of about 40 min to give 38.2 g of clear, colorless liquid (Sample 5, Table 1). PFIB was then removed by distillation through the column (vide supra) surmounted by a tap-water-cooled distillation head. Because preliminary experiments had shown that the PFIB starting material and the product tended to co-distill even when using a relatively efficient column, the removal of PFIB required a very slow distillation over several days, during which time the distillate and distilland were monitored by GLC analyses. PFIB which was uncondensed by the distillation head condenser was vented to the hood through a "Drierite" drying tube. For this process the pot temperature was gradually raised from about 36-55 °C while the vapor temperature in the distillation head tended to remain at 25-26 °C. Under these conditions, only fractions of a gram of distillate were collected daily; however, progress of the separation was also monitored by daily weighing of the distilland.

Final fractionation was began when distilland weight reached 23.5 g (Sample 6, Table 1), and three fractions were collected; their GLC analysis is shown in Table 2 along with that of the pot residue. Fractions 2 and 3 with a combined weight of 11.3 g and a bp of 45-47 °C (lit.<sup>3</sup> 47 °C), represent a yield of

15.2% without considering the amount of PFIB starting material that was not converted either to product or other compounds.

Table 1. GLC Analyses of Reaction and Work-Up Mixtures (Area %).

Component	PFIB (I)	Dimer (III)	Product (II)	Acetonitrile	Other
Retention Time (min)	1.1	2.3	3.1	8-12*	Various
Sample No. (See text)					
1	4.0	0.3	6.8	86.1	2.8
2	18.3	8.3	26.8	25.9	20.7
3	6.5	0.0	8.7	58.0	26.8
4	12.0	7.9	3.3	54.2	22.6
5	29.0	11.1	50.0	4.2	5.7
6	5.4	17.0	64.8	10.7	2.1

\*During several analyses temperature programming was varied after elution of the product peak to determine the effect on retention time of this component.

NMR (fraction 2) ( $\text{F}_3\text{C}^1\text{C}^2(\text{F}_3\text{C})=\text{C}^3(\text{F})\text{CN}$ ).

$^{13}\text{C}$  (ext TMS/ $\text{CHCl}_3$ ).

$\text{CF}_3$ :  $\delta$  's 119.3, 119.1;  $^1\text{J}_{\text{CF}} = 273$  Hz (q)

$\text{C}^2$ :  $\delta$  118.4;  $^2\text{J}_{\text{CF}} = 35$  Hz (m);  $^2\text{J}_{\text{CF}_3} = 16$  Hz (d)

$\text{C}^3$ :  $\delta$  140.5;  $^1\text{J}_{\text{C}^3\text{F}} = 276$  Hz (d)

CN:  $\delta$  107.2;  $^2\text{J}_{\text{CF}} = 44$  Hz (d)

$^{19}\text{F}$  (ext trifluoroacetic acid (TFA)). Positive shift indicates resonance is downfield relative to TFA.

$\text{C}^1\text{F}_3$ :  $\delta$  +16.5;  $\text{J}_{\text{cis}} = 23$  Hz (d);  $\text{J}_{\text{CF}_3} = 7.3$  Hz (q)

$\text{CF}_3$ :  $\delta$  +15.6;  $\text{J}_{\text{trans}} = 7.5$  Hz (d);  $\text{J}_{\text{CF}_3} = 7.1$  Hz (q)

$\text{C}^3\text{F}$ :  $\delta$  -17.5;  $\text{J}_{\text{cis}} = 23$  Hz (q);  $\text{J}_{\text{trans}} = 7.8$  Hz (q)

Table 2. GLC Analyses of Distillates and Residue (Area %).

Component			PFIB (I)	Dimer (III)	Product (II)	Acetonitrile	Other
Retention Time (min)			1.1	2.3	3.1	8.7	Various
Fraction Number	Boiling Point (°C)	Weight (g)					
1	22 - 45	0.7	28.4	0.1	70.1	1.3	0.2
2	45 - 49	8.9	1.7	0.5	95.5	2.2	0.1
3	49 - 30	2.4	0.2	3.5	90.6	5.5	0.2
Residue	-	8.4	0.1	88.2	0.0	5.4	6.3

Integration of these spectra and a proton spectrum indicated that Fraction 2 contained 95.7 mole percent of II, 3.2% of acetonitrile, and less than 1% of an unidentified, proton-containing impurity.

### 2.3 Identification of the "Dimer" (III).

The GLC retention time of the major component of the distillation residue corresponded to that of the component termed "dimer" shown in Tables 1 and 2. NMR analysis of this material gave the following:

$^{13}\text{C}$  (ext TMS/ $\text{CHCl}_3$ )

$\delta$  66.8;  $J = 29.4$  Hz;  $J = 3.6$  Hz (9 peaks), one saturated carbon, no directly bonded fluorines.

$\delta$  155.3;  $J = 290$  Hz (d), one carbon, one fluorine directly bonded.

$\delta$  119.7;  $J = 291$  Hz (q), four carbons with three fluorines each.

Other resonances highly overlapped between  $\delta$  110 and  $\delta$  120 (unsaturated carbons).

$^{19}\text{F}$  (ext TFA, + downfield)

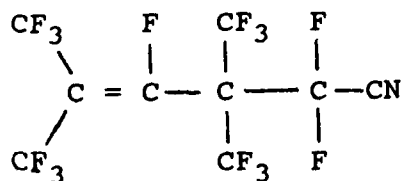
Spectra highly overlapped with no clear pattern.

Integration indicates:

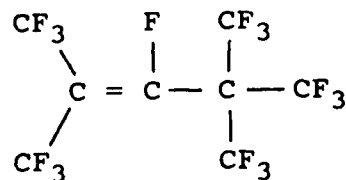
1 F:  $\delta$  1.25 (broad hump).

14-15 °F:  $\delta$  15.9 (multiplets)  $\text{CF}_3$  region.

These results, although not definitive because of the highly overlapped spectra with no clear pattern, may be interpreted as being generated by a compound having either structure (III) (most probable) or structure (IV).



(III)



(IV)

## 2.4 Reaction Optimization Study.

Preliminary experimentation indicated that long reaction times were detrimental to the yield of desired product. Further, after an initial and normal decrease in PFIB concentration, an increase in its level was noted. Accordingly, a reaction was carried out in which samples were withdrawn at 30-min intervals and promptly analyzed by GLC. The results of the analyses are shown in Table 3. It is interesting to note that the "dimer" (III) with a retention time of 2.3 min did not appear in these chromatograms.

Table 3. Changes in Reaction Mixture Composition with Time (GLC Analyses, Area %) (Solvent Area % Not Shown).

Component	PFIB (I)	Unknown* (III)	Product (II)
Retention Time (min)	1.1	1.7	3.1
<u>Samole No.</u>	<u>Min After KCN Addition</u>		
1	10	3.2	0.82
2	40	2.2	0.55
3	70	1.3	0.66
4	100	2.1	0.68
5	135	2.1	0.62

\*This impurity does not correspond to the "dimer" (III) which had a retention time of approximately 2.3 min.

## 3. DISCUSSION

### 3.1 General.

There are several aspects of the synthesis described herein which require comment. The original reference described treatment of PFIB with sodium cyanide in wet dioxane at 0 to -5 °C to give the disubstituted perfluoroacrylonitrile.<sup>3</sup> Although we attempted to use this procedure several times, the crude product was invariably water soluble and therefore not further investigated. It is of some interest to note that cooling to the designated temperature resulted in a virtually frozen reaction mixture. This is not surprising since 1,4-dioxane has a melting point (mp) of 11.8 °C; perhaps the investigators had used 1,3-dioxane (mp: -42 °C) but such was unnoted in their report, and the former solvent is customarily assumed when otherwise unspecified.

Our modification of the reaction, i.e., the use of anhydrous acetonitrile as solvent with a catalytic amount of 18-crown-6 ether to promote cyanide reactivity, was not without some disadvantages. It quickly became apparent that the highest concentration of desired product in the reaction mixture was a Gaussian rather than a plateau phenomenon. Reaction times longer than 1 hr resulted in dark intractable material which could be the tricyano substituted product if one accepts the previous investigators' implication that a dicyano compound is only formed in situ as a reactive intermediate.<sup>3</sup> Temporal optimization of product yield was possible inasmuch as the reaction could be quenched with cold, dilute sulfuric acid; however, conversion of the PFIB starting material was not complete. This incomplete conversion contributed to a problem of separation of product from the crude mixture resulting from the customary work-up procedures, in that a very carefully controlled and lengthy fractional distillation was required to remove the unreacted PFIB prior to product rectification.

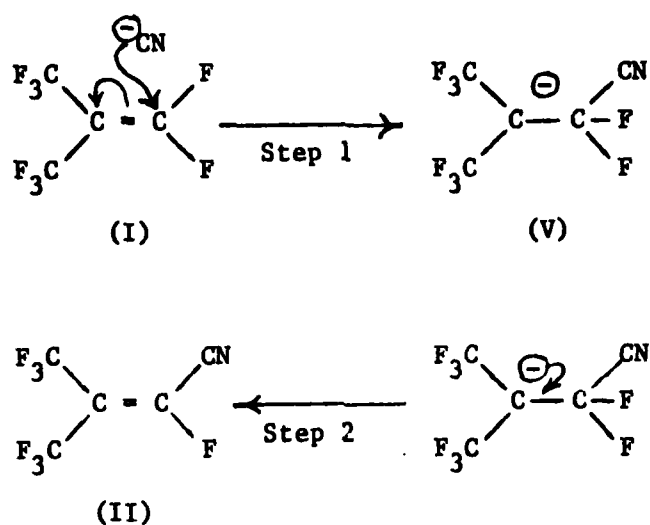
Another interesting aspect of this reaction was the appearance of a peak on the chromatograms between that of PFIB and the product. In such a case, one would normally expect a material of such retention time to have an intermediate boiling point. In this event, however, the material remained in the pot residue after fractionation and removal of the desired product, thus indicating a compound with a higher boiling point than expected; its yield approached that of the product itself. On the basis of NMR analysis it was tentatively identified as a condensation product of PFIB and the title compound. It is referred to in this report as the "dimer."

### 3.2 Possible Reaction Mechanisms.

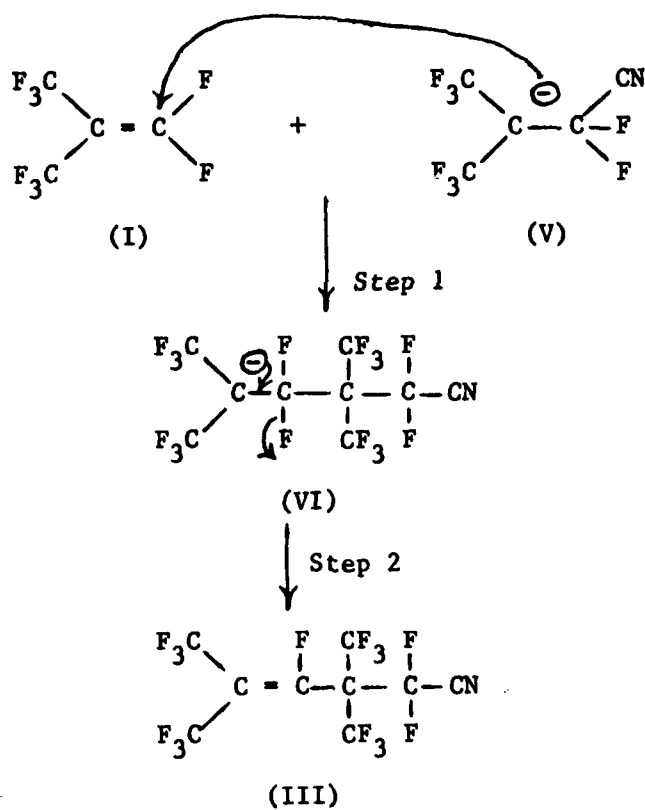
The nature of product (II) and byproduct (III) formation in the present case presents an opportunity for interesting mechanistic speculation. It is reasonable to expect that attack of cyanide ion at the gem-difluoro position of PFIB would produce the relatively stable carbanion V (Figure 1, Scheme 1, Step 1); a shift of electrons as in Step 2 would then give the product. The stability of V is related to the electron-withdrawing ability of the trifluoromethyl group (consider, e.g., the strength of trifluoroacetic acid). In this instance, anion stability would be considerably enhanced by the presence of two such groups.

The anion, V, is critical to one postulated mechanism of "dimer" formation. Attack of this moiety on unreacted PFIB would give an anion, VI (Figure 1, Scheme 2, Step 1), which could then collapse to III (Step 2). However, this is not the only potentially favorable mechanism for the formation of III. It is known that tetrafluoroethylene undergoes a (2 + 2) cycloaddition to give perfluorocyclobutane, and that other electron-withdrawing substituents on the ethylene molecule increase the reaction potential of this species through a diradical intermediate.<sup>5,6</sup> In the present instance, it is unnecessary to formulate a radical mechanism; and a radical initiator per se is not present to our





Scheme 1



Scheme 2

Figure 1. Possible Mechanisms of Formation of Product (II) and "Dimer" (III).

knowledge. Both the PFIB and the product anion (V) have gem-trifluoromethyl groups that could activate the incipient cycloaddition shown in Figure 2. In Step 1 of this mechanism, cyanide ion attacks the geminal difluoro carbon with a concomitant shift of electrons that results in the formation of the anion, VIII. Electronic rearrangement of the latter (Step 2) leads to the "dimer" (III).

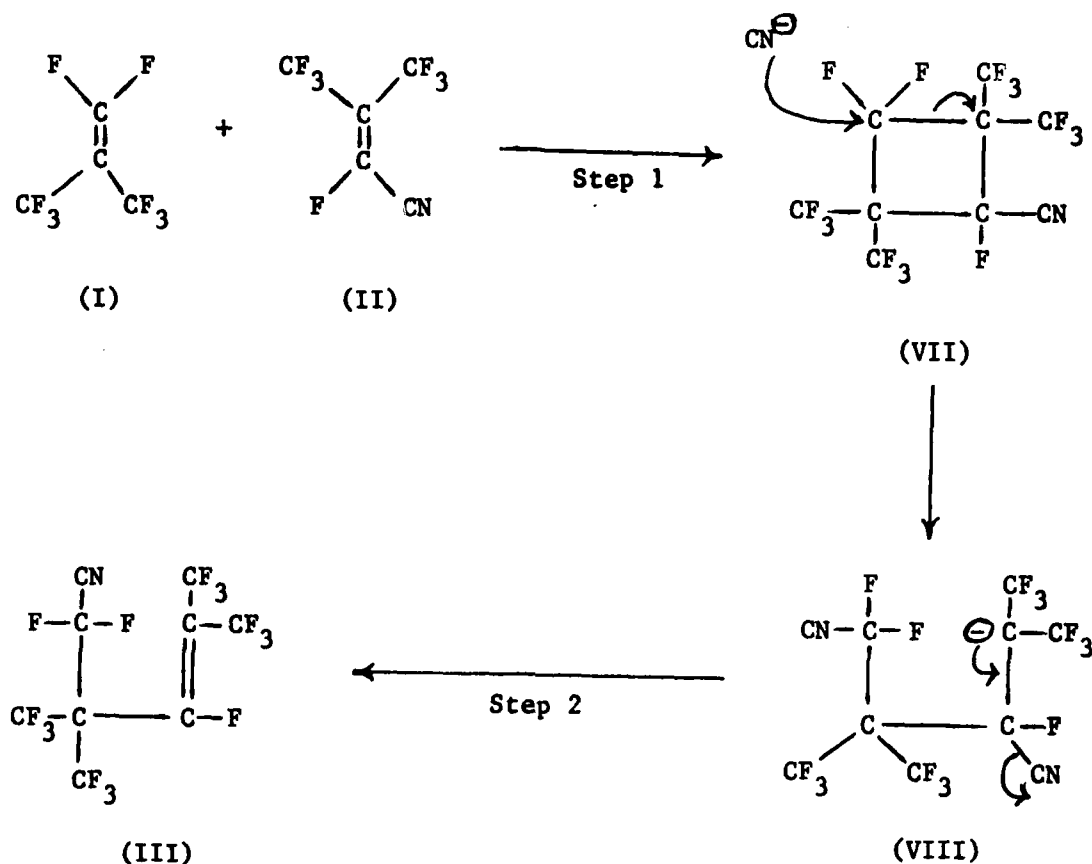
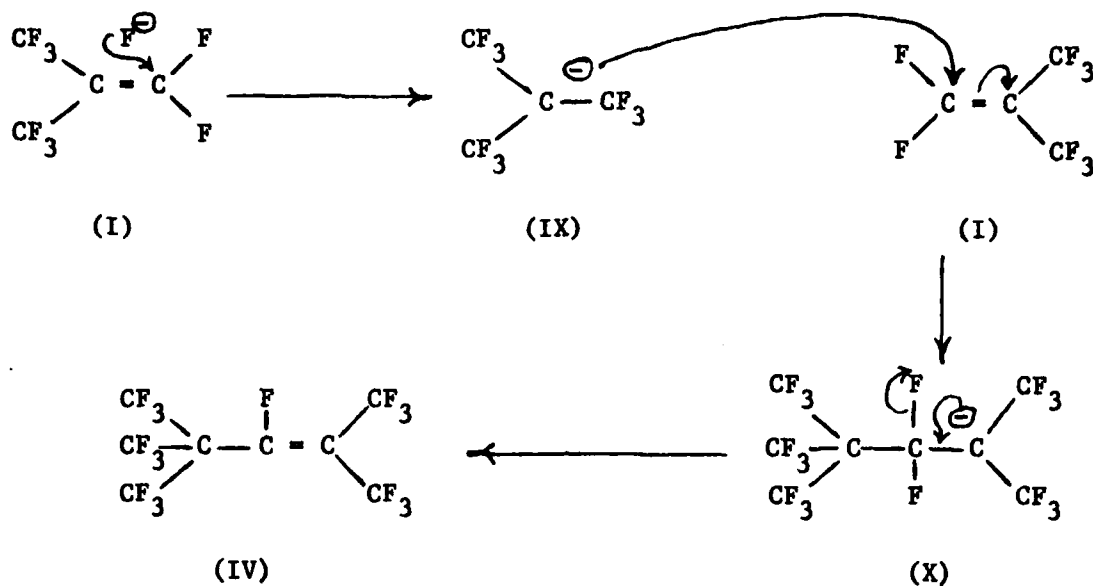
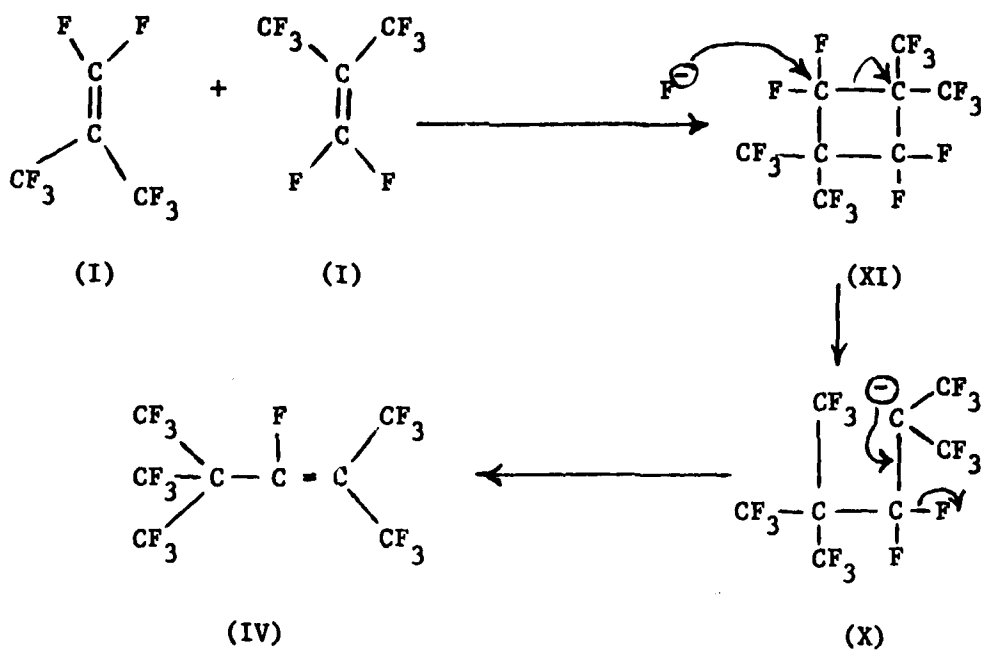


Figure 2. A Possible (2 + 2) Cycloaddition Reaction Mechanism for the Formation of "Dimer" (III).

The possibility of an alternative or additional byproduct having structure IV was suggested by the NMR spectrum of the distillate. Although it is probable that III is the predominant component, the availability and reactivity of the fluoride ion in the reaction mixture must be considered. In terms of nucleophilicity one would expect the cyanide ion to be more nucleophilic than the fluoride ion since each is the conjugate base of a weak and a strong acid, respectively. In this sense then, and on a qualitative basis, less byproduct of fluoride origin than of cyanide origin would be expected and such appears to be the case. In mechanistic terms, structure IV is readily rationalized. As shown in Figure 3, Scheme 1, the attack of the fluoride ion on PFIB gives



Scheme 1



Scheme 2

Figure 3. Possible Reaction Mechanisms for Formation of an Alternative Byproduct (IV).

the stabilized anion IX which subsequently reacts with another molecule of PFIB to give X, the anionic precursor of IV. As shown in Scheme 2 of Figure 3, a (2 + 2) cycloaddition process is also possible. The attack of the fluoride ion on the cyclo-adduct (XI) of two molecules of PFIB again gives the anionic precursor X which can then collapse to IV. Whether PFIB does condense with itself under the experimental conditions employed is not known, but assuming even a "loose" molecular complex (*vide infra*) is possible, coupled with the availability of the fluoride ion, the driving force of this mechanism would be the formation of X and its subsequent rearrangement to IV.

The mechanisms described above are consistent with the experimental results. The formation of II is unlikely by any process other than classical addition-elimination proceeding through a stabilized anion, in analogy to the E1cB or carbanion mechanism.<sup>7</sup> Once its concentration in the reaction mixture begins to build, the probability for "dimer" formation by either a carbanion or (2 + 2) cycloaddition process becomes feasible. The latter may well explain the difficulty in separating unreacted PFIB and II in the crude product isolated from the reaction mixture. At that point, the cyanide ion is no longer present, and the cycloaddition product of these compounds may be subject to a thermal or equilibrium-type reversal. The possibility that they may form a "loose" complex, possibly of a pro-charge-transfer type, should not be overlooked either since a formal cycloaddition may, indeed, require radical initiation or photochemical induction. This could explain the absence of "dimer" in the optimization study, particularly since this mixture was not subject to work-up procedures; but in this case neither dilution nor analytical sensitivity factors can be ruled out entirely. Ultimately, a kinetic study of the concentration profiles of the pertinent reaction species may be required to define the reaction path. But the possible mechanistic routes to the product and byproducts, as described above, do provide an initial basis for potential improvements of yield and reaction conditions.

It also appears necessary to limit the availability of the elimination-generated fluoride ion; to do this a fluoride "sink" is needed. Such a "sink" could be methanol, which solvates the fluoride ion by hydrogen bonding and thus prevents its further reaction; but necessary stoichiometry would have to be experimentally determined, and the overall effect of the alcohol on the product-forming reaction is not readily predictable. Another possible method would involve a cyanide-functionalized anion exchange resin as a source of this nucleophile. This reagent would limit the instantaneous availability of the cyanide ion, and through anion exchange, prevent further reaction of fluoride ion. Also, the role of the solvent as a primary influence in this synthesis cannot be minimized and therefore, acetone, the classical solvent for cyanation reactions, may be preferable in this case.

### 3.3 Mixture Separation.

The concept of a molecular association complex between PFIB and the product, if demonstrated in fact, would account for the problem of separating mixtures of those components containing substantial amounts of the former, under the experimental conditions employed. The greater than 40 °C difference in their boiling points at ambient pressure suggests that this should be a facile separation even in the absence of a distillation column. If the synthesis route cannot be further modified to insure complete conversion of the PFIB, then a low-temperature distillation apparatus may assist the recovery of unreacted starting material.

### 3.4 GLC Retention Times.

The apparently anomalous elution of the "dimer," viz., between PFIB and the product in the chromatograms, is a phenomenon occasionally seen in GLC chromatography. Although there are a number of factors which influence retention time including carrier gas flow rate, substrate loading on the column, nature of the support material, column temperature, and others, the most dominant is the liquid (substrate) phase since analytes are partitioned between it and the carrier gas. While the partition coefficients for specific compounds in respect to a carrier gas stream and a liquid phase can be determined, this was beyond the scope of this project. It is interesting, however, to draw a parallel with octanol/water partition coefficients which can be calculated for the analytes; actual values would certainly differ between systems but general trends should be consistent. The logarithm of the octanol/water partition coefficient ( $\log P$ ) was calculated<sup>8</sup> for PFIB ( $\log P = 0.850$ ), product (II) ( $\log P = 0.525$ ), and the "dimer" (III) ( $\log P = -0.045$ ). These values must be considered as preliminary since approximations were necessary for the vinyl group environment of II and III; however, a trend is evident. For a GLC liquid phase of intermediate polarity such as the Silastic 420 used in this work, one can, on the basis of the partition coefficients, expect elution of PFIB followed by the product, particularly in view of their boiling points of 5 and 47 °C, respectively. The intermediate retention time of the "dimer" is somewhat more difficult to explain for we know only that it has a considerably higher molecular weight than I or II, and its boiling point is above either but undetermined. Nevertheless, its partition coefficient is indicative of a very hydrophilic material and for the column used in these analyses it is reasonable to expect a relatively short retention time and, indeed, such was the observation.

## 4. CONCLUSIONS

Perfluoro- $\beta,\beta$ -dimethylacrylonitrile (II) can be prepared in modest yield by treatment of (PFIB) in acetonitrile solvent with potassium cyanide in the presence of 18-crown-6 ether catalyst.

Product (II) formation in the time course of the reaction follows a Gaussian rather than a plateau profile; maximum concentration occurs between 60 and 70 min with incomplete conversion of PFIB in the presence of a small stoichiometric excess of potassium cyanide.

A major byproduct of the reaction has been tentatively identified as 1,1,1,3,5,5-hexafluoro-2,4,4-trifluoromethyl-5-cyano-2-pentene (III), an apparent condensation product of PFIB and the title compound.

Reaction mechanisms consistent with the experimental results and which invoke a stabilized carbanion intermediate, can be proposed for both product and byproduct formation; byproduct formation could also proceed through a (2 + 2) cycloaddition reaction between PFIB and the title compound.

## 5. RECOMMENDATIONS

The unusual facets of the reaction described herein present several opportunities for investigations that could influence general methods for the synthesis of organofluorine compounds.

The extreme reactivity of "naked" anions formed through the mediation of crown ethers may not always be desirable nor reaction conditions or parameters appropriate for their use. It would be of interest to determine if a cyanide-functionalized anion exchange resin, possibly in a flow (as opposed to batch) system, could be utilized in this synthesis to limit instantaneous cyanide ion concentration as well as provide a "sink" for the generated fluoride ion.

The concentration profiles of the various constituents in the reaction could be characterized kinetically to give increased insight into reaction mechanisms and the potential for yield improvement or selective synthesis.

The possibility of cycloaddition or charge-transfer complex formation reactions between the organofluorine compounds utilized and produced in the reaction could be investigated from a mechanistic as well as synthesis method development viewpoint.

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